Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: the case of Plana de Vic (Osona, Spain).

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Abstract

This paper describes an integrated application of classical hydrogeological methods and multi-isotopic methods ($\delta^{15}N$, $\delta^{18}O_{NO3}$, $\delta^{34}S$, $\delta^{18}O_{SO4}$, $\delta^{13}C$) to assess the fate of groundwater nitrate in the Osona area, declared vulnerable to nitrate pollution by the Catalan Government in 1998, where nitrate is derived from intensive pig farming activities. Previous studies, involving a small area, indicated the occurrence of denitrification processes and their relationship with pyrite oxidation (Vitòria et al., 2008). For the present study, groundwater samples were collected at 60 production wells at three different periods between April 2005 and May 2006 to confirm that denitrification takes place in a larger area than that studied by Vitòria et al (2008). The aim of the study was to characterize the denitrification processes that control natural attenuation and to study their spatial and temporal variations. Nitrate concentration ranged from 10 to 529 mg/l, with 82% of the wells above the drinking water threshold of 50 mg NO_3/l. Nitrate isotopic composition ranged from +5.3‰ to +35.3‰ for $\delta^{15}N$ and from +0.4‰ to +17.6‰ for $\delta^{18}O_{NO3}$, and the samples showed a positive correlation between $\delta^{15}N$ and $\delta^{18}O_{NO3}$, with a $\varepsilon N/\varepsilon O$ ratio of 1.8, consistent with denitrification processes. The link between denitrification and pyrite oxidation is demonstrated by coupling chemical data with nitrate and sulfate isotopes. Furthermore, a spatial distribution of samples with significant denitrification was observed, allowing us to determine two main hydrogeological zones where natural attenuation was most effective. In several of the studied points, denitrification processes related to pyrite oxidation predominated and an estimation of the isotopic enrichment factors was performed using the temporal variations of nitrate concentration and the isotopic composition of dissolved nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$). Finally, using estimated

isotopic enrichment factors, an approximation of the degree of natural attenuation of nitrate was performed on those samples showing clear denitrification, and a median value of 30% of contaminant diminution was obtained.

Keywords: nitrate pollution, multi-isotopic, heterotrophic and autotrophic denitrification, pyrite oxidation.

1. Introduction

In the last decades, nitrate pollution has become a major threat to groundwater quality as the threshold value for drinking water (50 mg/l, EC, 1998) is being reached in most of the local and regional aquifers in Europe. The European Groundwater Directive (EC, 2006) considered nitrate as one of the main contaminants that could hamper the achievement of the goals of the Water Framework Directive (EC, 2000). High nitrate in drinking water poses a health risk because high nitrate ingestion can cause methemoglobinemia in infants and young children (Comly, 1945; Magee and Barnes, 1956). Some authors even point out that nitrogen compounds can act as human cancer promoters (Volkmer et al., 2005; Ward et al., 2005). Nitrate pollution is linked to the intensive use of synthetic and organic fertilizers, as well as to septic system effluents. In Catalonia, according to the European nitrate directive (EEC, 1991), nine areas have been declared vulnerable to nitrate pollution from agricultural sources (DOGC, 1998). One of the vulnerable areas with the highest nitrate concentration is the Osona area, where nitrate is derived from intensive pig farming activities. Even though the local administration regulates and controls the present use and distribution of manure as fertilizer, nitrate pollution in Osona shows the effect of decades of uncontrolled

manure application, which has resulted in nitrate contents in groundwater often exceeding 100 mg/l. This high nitrate content results in a loss of water availability for domestic uses in an area where precipitation is irregular and scarce and poses a threat to water management. To improve water management in those areas vulnerable to nitrate pollution, it is essential to understand the processes that control groundwater nitrate content. In the Osona region, multi-isotopic methods have been applied to identify the sources of nitrate and to determine the existence of denitrification processes (Vitòria et al., 2008).

Stable isotopes of dissolved nitrate are a powerful tool to study the denitrification processes. Stable isotopes are usually measured as the ratio between the desired isotope and the most-abundant one, e.g. ^{15}N against ^{14}N. Because measuring such a small difference cannot be feasibly done in an absolute way, these ratios are almost always established with respect to international standards. As a result, measures are usually expressed in delta notation (Eq.1),

$$\delta^{15}N = \frac{R_{sample} - (R)_{std}}{(R)_{std}} \times 1000 \text{ ; where R=}^{15}N/^{14}N \text{ ratio} \quad (1)$$

Denitrification, which consists of NO_3 reduction to N_2 under anaerobic conditions, is the main natural process to attenuate nitrate pollution in groundwater. During denitrification, as nitrate concentration decreases, residual nitrate becomes enriched in heavy isotopes ^{15}N and ^{18}O with a $\varepsilon N/\varepsilon O$ ratio that ranges from 1.3 (Fukada et al., 2003) to 2.1 (Böttcher et al., 1990). The isotope enrichment factor (ε) is defined (Eq. 2) as:

$$\varepsilon_{product} - \varepsilon_{reactant} = \frac{R_{product}}{R_{reactant}} - 1 \quad (x10^3‰) \quad (2)$$

The approximation $\varepsilon_{product} - \varepsilon_{reactant} \approx \delta^{15}N_{product} - \delta^{15}N_{reactant}$, can be used for the values

of ε and $\delta^{15}N$ usually found in natural abundance studies (Fritz and Fontes, 1980).

The analysis of nitrate for both $\delta^{15}N$ and $\delta\ ^{18}O$ has been useful for the identification of denitrification in groundwater (e.g. Aravena and Robertson, 1998). Moreover, the isotopic composition of dissolved nitrate has also been used to distinguish between dilution and denitrification in groundwater samples in areas where a decrease in nitrate concentration is observed (Grischek et al., 1998; Mengis et al., 1999; Cey et al., 1999).

A further step in the investigation of denitrification processes is to determine the processes governing the reaction. Denitrification refers to the microbiologically mediated process of reduction of nitrate. Two main denitrification reactions have been suggested to occur in aquifers: heterotrophic denitrification by oxidation of organic compounds and autotrophic denitrification by oxidation of inorganic compounds (Rivett et al., 2008). To determine the relative role of heterotrophic and autotrophic processes in denitrification of groundwater, several studies have used the coupled approach of chemical data with the $\delta^{15}N$ and/or $\delta^{18}O$ of dissolved nitrate and the isotopic composition of the ions involved in denitrification reactions, such as, for example, the $\delta^{34}S$ and $\delta\ ^{18}O$ of dissolved sulfate, and/or the $\delta^{13}C$ of dissolved inorganic carbon (Aravena and Robertson, 1998; Pauwels et al., 2000).

Vitòria et al. (2008) showed the occurrence of denitrification processes in a small area located in the northern part of the Osona region and suggested that sulfide oxidation had an important role in natural attenuation. A further step in the investigation of denitrification processes taking place in this area is the study of their spatial and temporal patterns. Spatial variations can be useful to distinguish factors controlling denitrification processes such as hydrogeological characteristics of the aquifer or

domestic withdrawal rates in order to identify where measures could be applied to avoid further deterioration in water quality. Likewise, knowledge of temporal trends in nitrate contents and denitrification processes is also valuable for the successful application of water-protection strategies. Therefore, the main purpose of our study was: 1) to confirm that denitrification takes place in a larger area than that studied by Vitòria et al. (2008), 2) to characterize the denitrification processes that control natural attenuation in this area, and 3) to study their spatial and temporal variations. To this end, groundwater was studied coupling classical hydrochemical data with a comprehensive isotopic characterization of the ions involved in denitrification reactions ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\delta^{13}C_{DIC}$).

2. Study area

The Osona region is located to the North of Barcelona, between Montseny Mountain and the pre-Pyrenees range. This study focuses on its eastern and central part, namely "Plana de Vic", an area of 600 Km^2 belonging to the Ter River basin. Figure 1 shows the studied area, which includes the smaller area characterized in Vitòria et al. (2008). The area has a sub-Mediterranean climate with an annual mean temperature of 13°C and potential evapotranspiration higher than rainfall, making Osona a dry area that mainly relies on groundwater resources to fulfill its agricultural and farming demand. During the studied period (from April 2005 to May 2006), potential evapotranspiration (estimated by Thornthwaite equation) was higher than rainfall except for the time between September 2005 and January 2006. In September 2005, the first significant rainfall event occurred after almost one year of a significant drought. Therefore,

samples collected in April 2005 and in May 2006 represent groundwater in a dry period and the samples of the October 2005 campaign, groundwater in a wet season.

From a geological perspective, this hydrogeological system lies on Paleogene sedimentary materials overlying Hercynian crystalline (igneous and metamorphic) rocks (Fig. 2a). The stratigraphic sequence primarily consists of carbonate formations, with an alternation of calcareous, marl and carbonate sandstone layers (Fig. 2b). These formations show a rather uniform dipping of about 7-10º to the west, with an antiform structure only at the northern limit. Locally, at the south-west of the studied area, a gypsum marine formation outcrops. Hydrogeologically, the system is made up of a series of confined aquifers located in the carbonate and carbonate-sandstone layers, whose porosity is mainly related to the fracture network. The marl strata act as confining layers, as observed in boreholes and hydrogeological prospecting. Nevertheless, fracture network in those marl layers where the sand content is high allows a vertical leakage between aquifer levels. The main production wells for agricultural demand usually reach depths of more than 100 m, searching for the more productive confined aquifers. Alluvial aquifers are scarce and generally non-productive in the area, except those located at the Ter River terraces.

According to a conceptual flow model of the hydrogeological system in the area (Menció et al., 2009), two main flow systems have been identified: a surficial system, corresponding to unconfined aquifers that are directly affected by manure spreads; and a deep system, corresponding to a semiconfined aquifer that is less vulnerable to direct nitrate leachate in natural conditions. The lack of well casing, unnecessary from a constructive point of view, allows for the mixing of waters of distinct qualities within the well, resulting in the extraction of low quality water and, even worse,

impoverishing water resources stored in the deeper aquifer layers. Moreover, a downward leakage occurring towards the deeper aquifers because of the fractured nature of the confining units facilitates the entrance of nitrate-rich surficial groundwater and a loss of quality resources. Menció et al. (2009) determined three zones in the "Plana de Vic" area according to its hydrogeological dynamics (Fig. 1): Zone 1, located in the northern part of the Ter River and comprising the northern recharge areas; Zone 2, corresponding to the recharge area located at the eastern margin of the "Plana de Vic" to the south of the Ter; Zone 3, corresponding to the centre of the "Plana de Vic" and the western reliefs, to the south of the Ter (see Fig. 1). These zones are used in the present study to describe chemical and isotopic features of the studied area and to study temporal and spatial variability of the attenuation processes.

Osona is classified as vulnerable to nitrate pollution from agricultural sources following the nitrate directive (EEC, 1991). In the "Plana de Vic", nitrate pollution is widespread, with a median concentration above 100 mg/l over the last six years. As described in detail in Vitòria et al. (2008), more than 10,000 t of N are produced as a result of intensive farming activity. Most of the manure is used as organic fertilizer. Synthetic fertilizers are applied in the areas surrounding villages, as the use of pig manure close to urban areas is forbidden. Regarding non-agricultural sources of nitrate, such as sewage or septic system leakage, the expected contribution is orders of magnitude lower than agricultural sources. This is mainly due to the fact that the total population is only 140,000 and 93% of the municipalities of the area are connected to sewage treatment plants, with nitrogen elimination treatment. On the other hand, sewage or septic system leakage is unlikely to cause such widespread diffused pollution.

3. Methods

Samples for chemical and isotopic characterization were collected in April 2005, October 2005 and May 2006 from 60 pre-existent production wells (Fig. 1), except for the May 2006 survey, when only 30 samples were gathered. Physicochemical parameters (pH, temperature, conductivity, dissolved O_2 and Eh) were measured in situ, using a flow cell to avoid contact with the atmosphere. Samples were collected after the wells had been continuously pumped until the Eh values became stabilized and stored at 4ºC. Chemical parameters (Cl^-, SO_4^{2-}, HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, total Fe, total Mn, NO_2^-, NO_3^-, NH_4^+ and TOC) were determined by standard analytical techniques.

The isotopic characterization included the nitrogen and oxygen isotopic composition of dissolved nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$), the sulfur and oxygen isotopic composition of dissolved sulfate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$), and the carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$). For the sulfur and oxygen isotopic analysis, the dissolved sulfate was precipitated as $BaSO_4$ by adding $BaCl_2 \cdot 2H_2O$ after acidifying the sample with HCl and boiling it in order to prevent $BaCO_3$ precipitation. For the $\delta^{13}C$ analysis, unfiltered samples were treated with a NaOH-$BaCl_2$ solution to precipitate carbonates, and then filtered at 3 μm. The $\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate were obtained following the denitrifier method of Sigman et al. (2001) and Casciotti et al. (2002). For the samples of the May 2006 campaign, nitrate analyses were performed using the anion exchange method (Silva et al., 2000, described in detail in Vitòria et al., 2008). Notation is expressed in terms of δ per mil relative to the international standards: V-SMOW (Vienna Standard Mean Oceanic Water) for $\delta^{18}O$, AIR (Atmospheric N_2) for

$\delta^{15}N$, V-CDT (Vienna Canyon Diablo Troillite) for $\delta^{34}S$ and V-PDB (Vienna Peedee Belemnite) for $\delta^{13}C$. The isotope ratios were calculated using international and internal laboratory standards. Reproducibility ($\equiv 1\sigma$) of the samples was determined as follows: ±0.3‰ for $\delta^{15}N_{NO3}$; ± 0.2‰ for $\delta^{34}S$; ± 0.5‰ for both $\delta^{18}O_{NO3}$, and $\delta^{18}O_{SO4}$; and ±0.2‰ for $\delta^{13}C_{DIC}$. Isotopic analyses were prepared at the laboratory of the Mineralogia Aplicada i Medi Ambient research group and analyzed at the Serveis Científic Tècnics of the Universitat de Barcelona, except for the isotopic composition of dissolved nitrates of some samples, which was analyzed at the Woods Hole Oceanographic Institution.

4. Results and Discussion

Median values of chemical parameters and stable isotopes of dissolved nitrate ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$), dissolved sulfate ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$) and dissolved inorganic carbon ($\delta^{13}C_{DIC}$) are summarized in Table 1, where groups are distinguished by zone and sampling survey. Bulk dataset is provided as supporting information (Appendix).

4.1. Nitrate sources and evidences of denitrification.

Nitrate concentration ranged from 10 to 529 mg/l with a median value of 127 mg/l (*n*=148). The percentage of studied wells with nitrate contents higher than the drinking water threshold of 50 mg/l was 85% in April 2005, 79% in October 2005 and 81% in May 2006. None of these wells correspond to the drinking water supply network. No clear relation between nitrate content and well depth was observed, due to the mix of waters within the wells, as they are uncased production wells. Menció et al. (2009) showed that there is also a downward leakage of nitrate towards the deeper aquifers due

to the recharge induced by intensive pumping of the surface aquifer layers, hindering the interpretation of chemical data.

In the studied area, $\delta^{15}N_{NO3}$ ranged from +5.3‰ to +35.3‰ with a median value of +13.4‰, and the $\delta^{18}O_{NO3}$ ranged between +0.4‰ and +17.6‰, with a median value of +4.5‰ (*n*=147). Isotopic values of the main nitrate sources in the studied area are thoroughly discussed in Vitòria et al. (2008). Most of the Osona samples with higher nitrate concentration showed $\delta^{15}N$ between +9.0‰ and +15‰, in agreement with manure or sewage values (Fig. 3a). Coupling nitrogen with oxygen values of dissolved nitrate, most samples are also within the range of manure or sewage-derived nitrate (Fig. 3b). Although the expected contribution from non-agricultural sources of nitrate —sewage or septic system leakage— was orders of magnitude lower than that from agricultural sources, nevertheless, to totally discard the role of sewage in nitrate pollution, the analysis of boron isotopes (Widory et al., 2004; 2005) should be applied in future research. Those samples with nitrate concentration below 100 mg/l showed higher variability, with $\delta^{15}N$ ranging from +5‰ to +35‰. The value of $\delta^{15}N$ of +5‰ ($\delta^{18}O_{NO3}$ = +3.2‰) corresponding to a well 200 m deep, showed the lowest NO_3^- and Cl^- concentrations in the studied area (SPT-010). The isotopic composition is in agreement with the isotopic signature of nitrate derived from mineralization of soil organic nitrogen (Heaton, 1986), thus representing a natural end-member.

$\delta^{15}N$ values between +15‰ and +35‰ could be explained either by volatilization or by denitrification (Fig. 3a), but the observed coupled increase of $\delta^{15}N$ and $\delta^{18}O$ (Fig. 3b) suggested that denitrification was taking place, hence discarding volatilization processes. During denitrification, as nitrate concentration decreases, residual nitrate becomes enriched in heavy isotopes ^{15}N and ^{18}O with a $\varepsilon N/\varepsilon O$ ratio that ranges from

1.3 (Fukada et al., 2003) to 2.1 (Böttcher et al., 1990). Intermediate enrichment ratios have been reported by Cey et al. (1999), Mengis et al. (1999), DeVito et al. (2000) and Lehman et al. (2003). In the studied samples, there is a positive correlation (r^2= 0.69) between $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, with a slope of 0.56. The observed slope shows that the enrichment for ^{15}N is higher by a factor of 1.8 than for ^{18}O. This value of 1.8 is in the range of reported results for denitrification in groundwater. Chemical parameters related to redox conditions indicated oxic conditions for most of the studied wells. Eh values varied from 116 mV to 490 mV, with a median value of 378 mV (*n*=123). Measured dissolved oxygen (DO) ranged from 0.8 mg/l to 16.3 mg/l, with a median value of 4.9 mg/l (*n*=90). Manganese was detected in few samples and contents were around 0.05 mg/l. Fe concentration ranged from 0.02 mg/l to 1.48 mg/l, with a median value of 0.08 mg/l (*n*=71). NO_2^- content varied from 0.01 mg/l to 3.89 mg/l, with a median value of 0.03 mg/l (*n*=66). NO_2^- is an intermediate step during denitrification processes. Although no clear correlation was observed between the NO_2^- values and $\delta^{15}N$ or $\delta^{18}O_{NO3}$, the median NO_2^- concentration for those samples with $\delta^{15}N$ > 15‰ was 24.5µg/l, and 4.5 µg/l for samples with $\delta^{15}N$ < 15‰. One requirement for denitrification is anaerobic conditions or restricted oxygen availability (dissolved oxygen concentration less than around 2 mg/L, e.g. Korom, 1992; Cey et al., 1999). Although in most of the studied wells (85%) dissolved oxygen concentrations were higher than 2 mg/L, indicating unsuitable conditions for denitrification to occur, isotopic data clearly showed the occurrence of natural attenuation. According to Koba et al. (1997) and Moncaster et al. (2000), denitrification can take place at higher dissolved oxygen concentrations because denitrification occurs in micro-anaerobic environments where dissolved oxygen has been completely removed.

4.3. Heterotrophic or autotrophic denitrification?

Denitrification processes take place under reducing environments, usually in the saturated zone. This process is linked either to organic matter oxidation or to sulfide oxidation. The reactions controlling the denitrification process can be revealed, to some extent, by studying chemical data coupled with the isotopic composition of the solutes involved in the reactions: $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, $\delta^{13}C_{DIC}$, $\delta^{18}O_{H2O}$, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. Denitrification by oxidation of organic matter should result in a decrease of nitrates together with a HCO_3 increase. Isotopically speaking, an increase in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ coupled with a decrease in $\delta^{13}C_{DIC}$ is expected (Eq. 3).

$$4NO_3^- + 5C + 2H_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 \quad (3)$$

Pyrite could also act as an oxidant agent, as has been proposed in other aquifers based on geochemical data (Kölle et al., 1983; Böttcher et al., 1990; Postma et al., 1991; Engesgaard and Kipp, 1992; Robertson et al., 1996; Cravotta, 1998; Pauwels et al., 1998; Schwientek et al., 2008). Denitrification by sulfide oxidation takes place in several steps (Eq. 4, 5, 6):

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4Fe^{2+} + 8SO_4^{2-} + 8H^+ \quad (4)$$

$$10Fe^{2+} + NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H_2O \quad (5)$$

$$6NO_3^- + 2FeS_2 + 2H_2O \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+ \quad (6)$$

Though it is believed that denitrification by sulfide oxidation cannot occur in carbonated aquifers where pH is higher than 7, nevertheless, if the Fe^{2+} produced is oxidized, following reaction 5, a global reaction 6 can be written where protons could

locally exceed those consumed by carbonate dissolution (Moncaster et al., 2000). If this is the case, denitrification by pyrite oxidation could occur in a carbonate aquifer. Denitrification by sulfide oxidation should result in an increase in SO_4^{2-} coupled with a decrease in NO_3^-. Isotopically, an increase in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ is expected and $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ should match with the isotopic composition of sulfates derived from sulfide oxidation.

The $\delta^{34}S$ of the dissolved sulfate ranged from -19.5‰ to +9.3‰, with a median value of -4.4‰ (*n*=149), and the $\delta^{18}O_{SO4}$ varied from -1.1‰ to +9.0 ‰, with a median value of +4.0‰ (*n*=147). Negative sulfur values can be explained by sulfide oxidation. Disseminated pyrite in marls in the area had $\delta^{34}S_{FeS2}$ ranging from -5‰ and -28‰ (Pierre et al., 1994). 46% of the studied samples showed $\delta^{34}S_{SO4}$ values within this range. As is explained in detail in Vitòria et al. (2008), the $\delta^{18}O$ of sulfates formed via sulfide oxidation must show a relationship with $\delta^{18}O_{H2O}$. Indeed, 83% of the studied samples fall within the experimental area of sulfates derived from sulfide oxidation defined by Van Stempvoort and Krouse (1994) (Fig. 4a). Figure 4b shows the main sulfate sources in the area and the studied samples, which plot within an area between sulfate from sulfide oxidation and positive $\delta^{34}S$ end members: manure sulfate, soil sulfate, fertilizers and evaporites. Due to the absence of major evaporite rock outcrops in the area, the positive sulfur values could be explained in terms of anthropogenic sources linked to agricultural and livestock raising activities (see details in the following section). Only the groundwater recharging in the western reliefs, in the south-western part of Zone 3, could interact with locally outcropping gypsum layers, and thus acquire a different isotopic signature (e.g. samples TON-001, TON-006, TON-007, TON-008, VIC-004 and VIC-007, see Appendix). In a $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram, samples plot in

a mixing line between the isotopic composition of sulfate originated from pyrite oxidation ($\delta^{34}S$ values < -5‰) and the isotopic composition of pig manure ($\delta^{34}S_{SO4}$ values from 0 to +5‰, Otero et al., 2007; and $\delta^{15}N_{NO3}$ values between +8‰ and +15‰, Vitòria et al., 2004a), suggesting a link between pyrite oxidation and denitrification. Moreover, samples with clear denitrification ($\delta^{15}N_{NO3}$ > 15‰) correspond to samples with sulfate from pyrite oxidation, confirming the role of pyrite oxidation in denitrification (Fig. 5).

To evaluate the relative role of organic matter oxidation in the natural nitrate attenuation, nitrate isotopes were studied coupled with $\delta^{13}C_{DIC}$ and bicarbonate concentrations. In the studied area, due to the aquifer lithology, which consists mainly of carbonate formations, groundwater has a high natural bicarbonate concentration (up to 576 mg/l, with a median value of 407 mg/l) that could buffer the isotopic composition of $\delta^{13}C_{DIC}$. Measured $\delta^{13}C_{DIC}$ varied from -15.5‰ to -9.2‰, with a median value of -12.5‰ (*n*=146), except for two samples with higher values (GRB-118 with -7.6‰, and SVT-004 with -6.9‰ and -7.4‰). These values are in agreement with the known range of $\delta^{13}C_{DIC}$ for groundwater (-16‰ to -11‰, Vogel and Ehhalt, 1963). No clear trend was detected between carbon concentration and isotopic composition (Fig. 6) making it difficult to study the role of organic matter oxidation in the denitrification.

4.4. Spatial variations of denitrification processes

The highest nitrate contents were detected in Zone 3, where the main crop fields are located and, consequently, where manure application is higher. In the recharge areas (Zones 1 and 2) manure application is less intensive, resulting in lower nitrate concentration in groundwater. The evidence of denitrification and the reactions involved

in the denitrification processes were studied for each area, coupling chemical with isotopic data.

In a $\delta^{15}N$ vs. $\delta^{18}O_{NO3}$ diagram (Fig. 3b), samples of Zone 1 follow a εN/εO ratio of 1.7 (r^2=0.73), indicating that denitrification is taking place. 33% of the samples (16 samples) can be considered clearly denitrified ($\delta^{15}N$ > +15‰ and $\delta^{18}O$ > +5‰). In the $\delta^{34}S$ vs. $\delta^{18}O_{SO4}$ diagram (Fig. 4b), all samples, except TOR-004, are in a mixing line between manure sulfate and sulfate from sulfide oxidation, indicating the role of pyrite in denitrification. TOR-004 can be explained by a ternary mix between sulfate from gypsum, sulfate from fertilizers and sulfate from pig manure. Moreover, in a $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram (Fig. 5), all the samples considered clearly denitrified ($\delta^{15}N$ > +15‰) had low $\delta^{34}S$ (ranging from -3.7‰ to -18.4‰), confirming the fact that denitrification was taking place through pyrite oxidation. Negative $\delta^{34}S$ did not necessarily imply high $\delta^{15}N$ since sulfide oxidation could take place by consuming the O_2, and not be related to denitrification (e.g. sample TOR-002). No clear relation was observed between HCO_3^- and either $\delta^{15}N_{NO3}$ or $\delta^{18}O_{NO3}$, making it difficult to study the role of organic matter oxidation in denitrification.

In Zone 2, there was a linear correlation between $\delta^{15}N$ and $\delta^{18}O_{NO3}$, pointing out the occurrence of denitrification processes (Fig. 3b), except for sample SJV-004 that had higher $\delta^{18}O_{NO3}$ values. However, only two samples (SEB-015 and SEB-018) can be considered clearly denitrified ($\delta^{15}N_{NO3}$ > +15‰ and $\delta^{18}O_{NO3}$ > +5‰). Therefore, in this zone denitrification processes are not widespread and only local points show clear signs of denitrification.

In the samples of Zone 3, $\delta^{15}N_{NO3}$ showed a positive correlation (r^2 = 0.65) with

$\delta^{18}O_{NO3}$, with a slope of 0.51, giving a εN/εO ratio of 2.0, indicating the occurrence of denitrification processes (Fig. 3b). 24% of these samples can be considered to be clearly denitrified ($\delta^{15}N_{NO3}$ > +15‰ and $^{18}O_{NO3}$ > +5‰). In denitrification processes, a linear relationship is expected when plotting $\delta^{15}N$ or $\delta^{18}O_{NO3}$ vs. ln [NO_3^-] (Mariotti, 1981; Böttcher et al., 1990; Fukada et al., 2003). In the studied case, due to the continuous nitrate inputs, the initial concentration and isotopic composition of percolated water in the recharge areas could differ depending on volatilization processes and rates of application. However, by using the NO_3^-/Cl^- ratio the effects of continuous nitrogen inputs could be averted. A positive correlation is observed between ln (NO_3^-/Cl^-) and both $\delta^{15}N$ (Fig. 7a) and $\delta^{18}O_{NO3}$ (data not shown), with correlation coefficients of 0.44 and 0.41, respectively, confirming the occurrence of denitrification processes. In a $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram (Fig. 5), several of the samples considered to be clearly denitrified ($\delta^{15}N$ > +15‰) had low $\delta^{34}S$ values, indicating a link between sulfide oxidation and denitrification. The sulfur isotopic signal of those samples clearly denitrified, but with $\delta^{34}S_{SO4}$ higher than -5‰, can be explained by the influence of the gypsum sulfate signature, as is confirmed in Fig. 4b, where samples from Zone 3 fall in the mixing field between sulfate from sulfide oxidation, sulfate from pig manure and sulfate from gypsum. The role of organic matter oxidation could neither be confirmed nor discarded. A positive trend between HCO_3^- concentration and both $\delta^{15}N_{NO3}$ (r^2=0.37; Fig. 7b) and $\delta^{18}O_{NO3}$ (r^2=0.38; data not shown) was observed, except for TON-001, suggesting an increase in HCO_3^- concentration due to denitrification by organic matter oxidation. On the other hand, a negative trend between $\delta^{34}S$ and the HCO_3^- concentration was also detected. Aravena and Robertson (1998) proposed that if denitrification by pyrite oxidation occurs, the acidity generated in the reaction tends to dissolve carbonates producing an increase in HCO_3^- concentration. Therefore, the

HCO_3^- increase could also be related to pyrite oxidation. As there was no clear correlation between $\delta^{13}C_{DIC}$ and the HCO_3^- concentration (data not shown), the two hypotheses are thus possible.

5.4. Temporal variability of denitrification processes

To study the temporal evolution of denitrification processes, multipiezometer wells and/or wells located along a groundwater flow line have been used (Mariotti et al., 1988; Böttcher et al., 1990; Postma et al., 1991; Aravena et al., 1993; Aravena and Robertson, 1998). Considering that in the studied area production wells do not coincide with a specific groundwater flow direction and that the lack of well casing causes the simultaneous exploitation of different aquifer layers, the evolution of denitrification processes in the Osona area was studied using the temporal variations of chemical and isotopic composition of each individual well. Moreover, it is necessary to taking into account that the isotopic and chemical composition of a sample reflects the balance between the entry of new nitrate, denitrification and mixing processes.

No significant changes in $\delta^{15}N_{NO3}$ values along the studied period were observed in 75% of the studied samples. However, in some of the samples it was possible to identify temporal changes in the isotopic and chemical compositions. Taking into account these temporal variations, four groups were distinguished:

- 40% of the samples showed no significant changes in nitrate concentration or isotopic composition.
- 32% of the samples showed a significant increase in NO_3^- concentration but with no changes in the isotopic composition. This means additional nitrate inputs in the system, with a similar isotopic composition, thus producing no changes in

groundwater isotopic values. All of these samples had $\delta^{15}N_{NO3}$ in the range of manure nitrate (from +10‰ to +15‰).

- Samples MNL0-19, SMC-010, GRB-106, TON-001, TON-008, VIC-103 and VIC-004 increased their nitrate content between April 2005 and May 2006, although $\delta^{15}N$ of dissolved nitrate decreased (see Appendix). Starting values in April 2005 were in the range of denitrification ($\delta^{15}N_{NO3}$ > +15‰). A decrease in $\delta^{15}N_{NO3}$ indicated that the entry of new nitrate was more important than the reduction of nitrate by denitrification processes.
- Samples LMV-005, ORI-001, MAL-001, SEB-015 and SEB-017 showed a $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ increase, coupled with a decrease in the $\delta^{34}S$ of dissolved sulfate between April 2005 and October 2005 (see Appendix). Moreover, these samples had $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values indicating clear denitrification. Denitrification processes related to pyrite oxidation predominated, causing a decrease in the nitrate content and an increase in the concentration of dissolved sulfate.

5.5. Estimation of the enrichment factors related to denitrification

The denitrification reaction describes a Rayleigh distillation process (Eq. 7 and 8) where ε is the isotopic enrichment factor that depends on the aquifer materials and characteristics (Mariotti et al., 1981).

$$\delta^{15}N_{residual} = \delta^{15}N_{initial} + \varepsilon_N \ln ([NO_3^-]_{residual} / ([NO_3^-]_{initial}) \quad (7)$$

$$\delta^{18}O_{residual} = \delta^{18}O_{initial} + \varepsilon_O \ln ([NO_3^-]_{residual} / ([NO_3^-]_{initial}) \quad (8)$$

According to these equations, the $\delta^{15}N$ and $\delta^{18}O$ of the dissolved nitrate increase

proportionately to the logarithm of the residual nitrate fraction. An estimation of the enrichment factors was performed using Equations 7 and 8 in those samples in which, between April 2005 and October 2005, denitrification processes related to pyrite oxidation predominated, causing increases in both $\delta^{15}N$ and $\delta^{18}O$ of nitrate and in dissolved sulfate concentration, and decreases in $\delta^{34}S_{SO4}$ and nitrate content (LMV-005, ORI-001, MAL-001, SEB-015 and SEB-017). Estimated enrichment factor are detailed in Table 2. The obtained values of enrichment factors for nitrogen (between -4.4‰ and -15.5‰ with a median value of -7.0‰) fall well within the range of values reported for denitrification in groundwater (-4.0‰ for Pauwels et al., 2000; -4.7‰ for Mariotti et al., 1988; -10.0‰ for Spalding and Parrott, 1994; -15.9‰ for Böttcher et al., 1990; and -30.0‰ for Vogel et al., 1981). Only three values of ε_O were found in the literature: -8.0‰ (Böttcher et al., 1990), -9.8‰ (Fukada et al., 2003), and -18.3‰ (Mengis et al., 1999). Values of estimated ε_O for the Osona aquifer range between -8.9‰ and -1.9‰, with a median value of -4.6‰. The $\varepsilon N/\varepsilon O$ ratio ranges between 0.9 and 2.3, which is also in agreement with literature values: from 1.3 (Fukada et al., 2003) to 2.1 (Böttcher et al., 1990).

Once the enrichment factor in a determined area is well characterized, the percentage of denitrification can be estimated on the basis of isotopic characterization (Eq. 9), using either ε_N or ε_O, or both.

$$DEN(\%) = \left[1 - \frac{[NO_3]_{residual}}{[NO_3]_{initial}}\right] * 100 = \left[1 - e^{\left(\frac{\delta_{(residual)} - \delta_{(initial)}}{\varepsilon}\right)}\right] * 100 \qquad (9)$$

In the studied area, using the median values of the obtained enrichment factors for nitrogen and oxygen (-7.0‰ and -4.6‰, respectively, *n*=5), a rough estimation of the

degree of attenuation can be calculated, following Equation 9, assuming an initial isotopic composition of $\delta^{15}N_{NO3}$ = +15‰ and $\delta^{18}O_{NO3}$ = +5‰ and using isotopic data of the studied wells as the composition of the residual nitrate. In that way, 75% of the samples had isotopic values in the range of manure. These samples were not considered to be clearly denitrified and, consequently, were discarded for the calculations. Based on both ε_N and ε_O, the natural attenuation in the remaining 25% of the studied samples varied between 0 and 60%, except for three samples (TON-001, MNL-019, and LMV-005) with denitrification higher than 75% (Fig. 8). Using the estimated enrichment factor for nitrogen, in those samples considered clearly denitrified, the median denitrification (Eq. 9) was found to be 33% (*n*=38); using εO, the median percentage of denitrification was found to be 25% (*n*=60). Fig. 8 shows the histograms of the percentages of denitrification, calculated using the ε_N of samples from Zones 1 and 3. Obtaining real enrichment factors of the aquifer in further laboratory experiments will allow to quantify a more realistic degree of natural attenuation of nitrate-contaminated groundwater in the studied area.

5. Conclusions

A multi-isotopic approach has successfully traced the sources of contamination and the processes affecting nitrate attenuation in groundwater in an area such as Osona, with complex and/or poorly studied hydrodynamics, where sampling relies on production wells and with a lack of an adequate infrastructure to monitor the fate of contaminants. Previous results obtained in a smaller area were confirmed, that is, that nitrate pollution in the Osona area is mainly derived from the application of pig manure as organic

fertilizer and that the use of synthetic fertilizers has a minimum contribution. The occurrence of denitrification processes in groundwater in the area was linked to pyrite oxidation, as demonstrated by coupling nitrate with sulfate isotopic data.

The relative roles of organic matter and pyrite in natural nitrate attenuation are different according to the distinct hydrogeological settings of the studied area. In that way, in Zone 1 denitrification by sulfide oxidation occurred in one third of the studied samples. In Zone 2 most of the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values were within the field of manure, and the occurrence of denitrification processes was limited to two samples. In Zone 3 denitrification takes place by sulfide oxidation in 24% of the samples, and although some relationships suggested that the oxidation of organic matter could also contribute to denitrification, its role is still unclear.

25% of the samples showed a clear denitrification trend throughout the studied period. Nitrogen and oxygen isotopic enrichment factors were estimated using observed temporal variations of nitrate concentration and isotopic composition (ε_N= -7.0‰ and ε_O= -4.6‰). An approximation to the extent of natural attenuation was calculated, showing a median value between 25% and 33%, though further laboratory work will be required to obtain the actual enrichment factors for the aquifer. Future work should focus on the study of the kinetics of denitrification by pyrite oxidation. It should also point out distinct areas in which different management options (from manure rate application to bioremediation actions) could be used to improve ground water quality.

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Appendix. Supplementary data.

Dataset including the chemical and isotopic data of the 3 surveys (April 2005, October 2005 and May 2006).

Figure captions

Figure 1. Studied area, showing land uses, sampling sites, and zones. The map includes the area characterized in Vitòria et al. (2008).

Figure 2. a) Simplified geologic map of the study area (Menció et al. 2009). Legend: Paleozoic: (1) Igneous rocks, (2) Metamorphic rocks; Mesozoic: (3) Sedimentary rocks; Paleogene: (4) Coarse detritic sandstones and conglomerates (Vilanova and Romagats Fms.), (5) Carbonates (Tavertet Fm.), (6) Sandstone, silt and marl (Bellmunt, Folgueroles, Artès Fms.), (7) Marls and marly sandstones (Banyoles, Igualada, and Vespella Fms.), (8) Evaporitic (gypsum) deposits; Quaternary: (9) Alluvial and other recent undifferentiated formations; (A) Faults, (B) Syncline and anticline folding. b) Geological cross-sections of the main geological formations in the study area. (Menció et al.2009). See Figure 2a for locations.

Figure 3. a) Nitrate concentration vs. $\delta^{15}N$ of the studied samples. b) $\delta^{15}N$ vs $\delta^{18}O_{NO3}$, together with the isotopic composition of the main nitrate sources in the studied area (Mengis et al. 2001; Vitòria et al., 2004b; Vitòria et al., 2008). Values of $\delta^{18}O$ of nitrate derived from nitrification of NH_4 of manure were calculated following experimental expressions of Anderson and Hooper (1983) and Hollocher (1984), using the range of $\delta^{18}O_{H2O}$ of the studied area (from -8‰ to -5.1‰, with a median value of -6.7‰,

n=149) and $\delta^{18}O_{O2}$ equals to +23.5‰ (Kroopnick and Craig, 1972; Horibe et al., 1973).

Figure 4. a) $\delta^{18}O_{H2O}$ vs. $\delta^{18}O_{SO4}$ diagram, the experimental area of sulfates derived from sulfide oxidation as defined by Van Stempvoort and Krouse (1994). b) $\delta^{34}S_{SO4}$ vs. $\delta^{18}O_{SO4}$ of dissolved sulfate, the box represents the sulfates derived from sulfide oxidation. Values for pig manure are taken from Otero et al. (2007) and Cravotta (1997), soil sulfate data from Clark and Fritz, (1997), fertilizer data from Vitòria et al. (2004b), and Gypsum values from Utrilla et al. (1992).

Figure 5. $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram. The shaded box represents the isotopic composition of pig manure (Vitòria et al., 2004a; Otero et al., 2007). Samples of Osona groundwater plot in a mixing line between the isotopic composition of sulfate originated from pyrite oxidation (with $\delta^{34}S$ values < -5‰) and the isotopic composition of pig manure sulfate. Moreover, samples with clear denitrification (with $\delta^{15}N_{NO3}$ > +15‰) correspond to samples with sulfate from pyrite oxidation.

Figure 6. HCO_3^- concentration vs. $\delta^{13}C$ of the studied samples. The usual range of $\delta^{13}C_{DIC}$ in groundwater (Vogel and Ehhalt, 1963) is also represented (dotted lines).

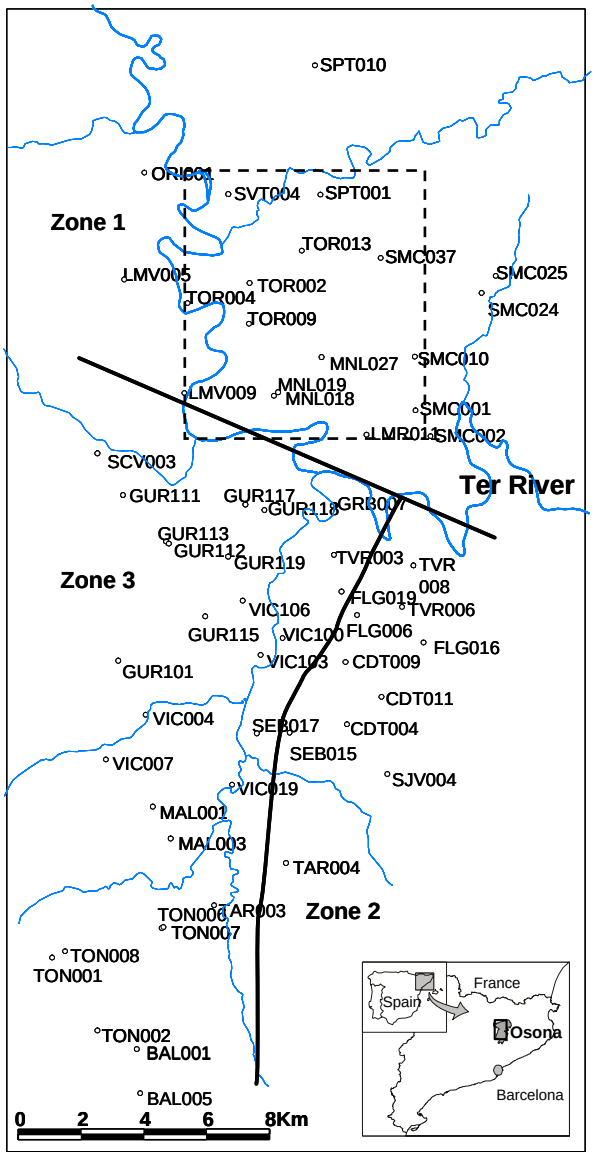
Figure 7. Samples from Zone 3. a) ln (NO_3^-/Cl^-) vs. $\delta^{15}N_{NO3}$. b) HCO_3^- concentration vs. $\delta^{15}N_{NO3}$.

Figure 8. Estimation of the percentage of natural denitrification taking place in the studied area, quantified in terms of the estimated isotope enrichment factors (the median values of calculated ε_O and ε_N are used). Histograms of the percentage of denitrification, calculated using the $\varepsilon_{N,}$ of samples from Zones 1 and 3.

Table 1. Median values of chemical and isotopic data. Groups are distinguished by zone and sampling survey.

Table 2. Estimation of the enrichment factors for N and O associated with the natural denitrification processes.

Figure 1


SPT010
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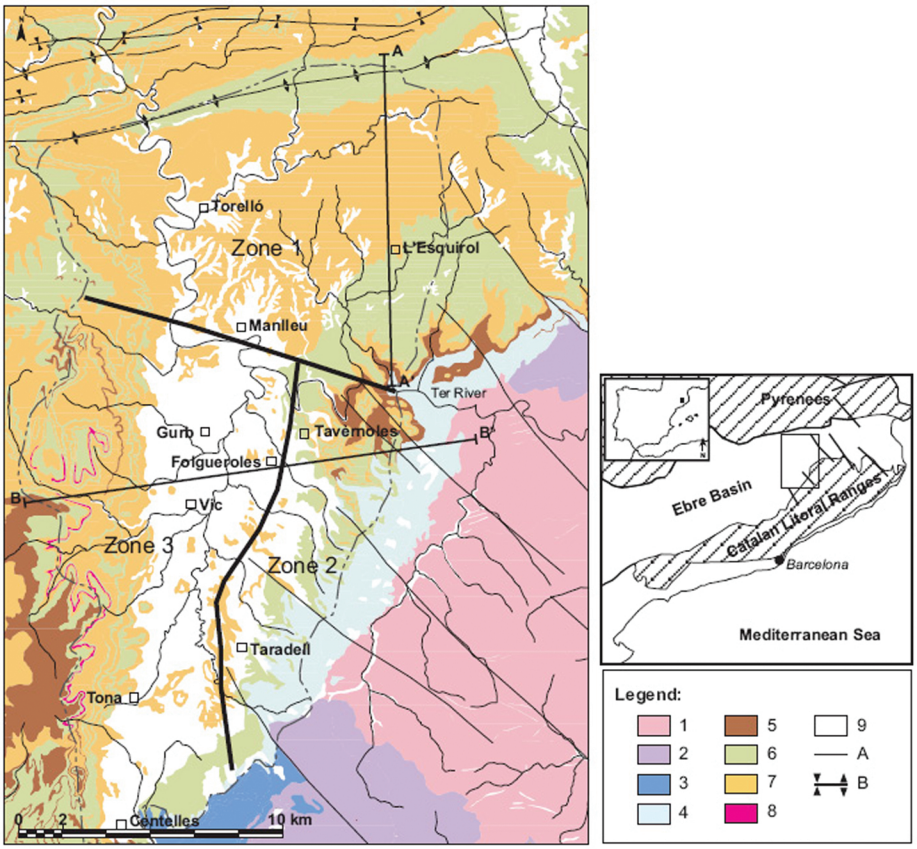
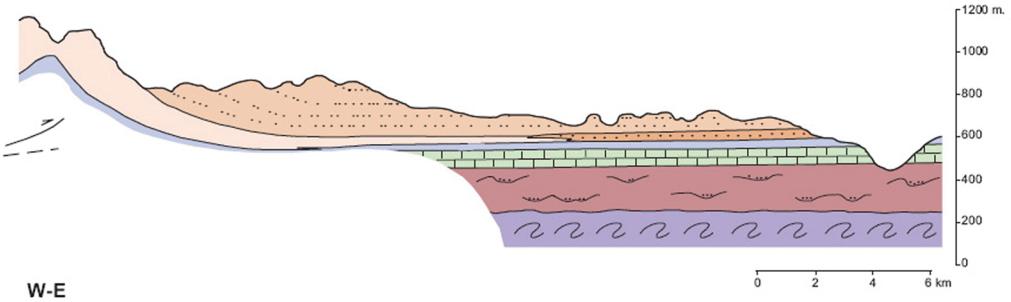
MNL018
SMC001
LMR014
SMC002
SCV003
Ter River
GUR111
GUR117
GUR118
GRB007
GUR113
GUR112
GUR119
TVR003
TVR 008
Zone 3
FLG019
VIC106
TVR006
GUR115
VIC100
FLG006
FLG016
VIC103
CDT009
GUR101
CDT011
VIC004
SEB017
CDT004
SEB015
VIC007
SJV004
VIC019
MAL001
MAL003
TAR004
TON006
TAR003
Zone 2
TON007
TON008
TON001
TON002
BAL001
BAL005
0 2 4 6 8Km
France
Spain
Osona
Barcelona


A
Torelló
Zone 1
L'Esquirol
Manlleu
A'
Ter River
Gurb
Tavèrnoles
B
Folgueroles
B'
Vic
Zone 3
Zone 2
Taradell
Tona
Centelles
0
2
10 km
Pyrenees
Ebre Basin
Catalan Litoral Ranges
Barcelona
Mediterranean Sea
Legend:
1
2
3
4
5
6
7
8
9
A
B

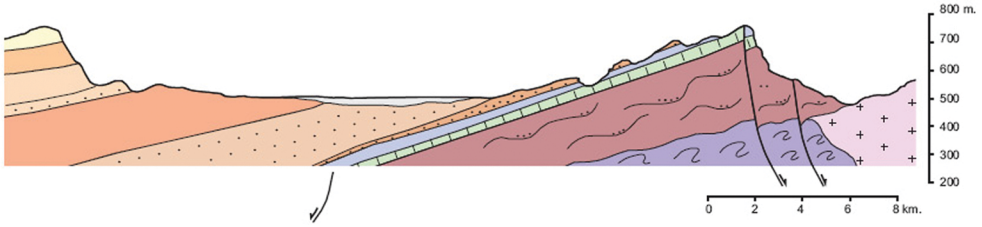
N-S

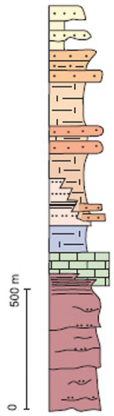
A-A'



W-E

B-B'





LEGEND.

Quaternary

- Alluvial and indiferentiated sedimentary materials.

Paleogene

- Sandstones and silt (Artès Fm.)
- Sandstones, marls, and silt (Upper Vespella Fm.)
- Marls and marly-sandstone (Middle Vespella Fm.)
- Sandstones, and marls (Lower Vespella Fm.)
- Marly-sandstones, and sandstones (Igualada Fm.)
- Sandstone, conglomerates and silt (Folgueroles Fm.)
- Sandstone, conglomerates and silt (Bellmunt Fm.)
- Marls, and sandy-marls (Banyoles Fm.)
- Limestones and marly-limestones (Tavertet Fm.)
- Silicic conglomerates and sandstones (Vilanova and Romagats Fms.)

Paleozoic

- Schists and shales.
- Granites.

Figure 3

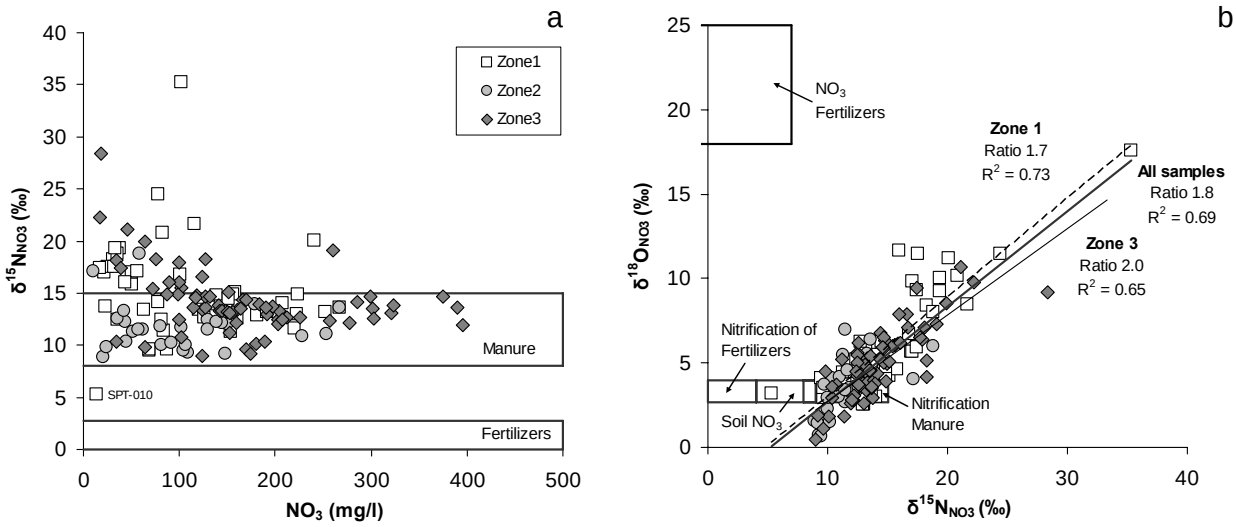

a
Zone1
Zone2
Zone3
Manure
SPT-010
Fertilizers
δ15NNO3 (‰)
NO3 (mg/l)
b
NO3 Fertilizers
Zone 1
Ratio 1.7
R2 = 0.73
All samples
Ratio 1.8
R2 = 0.69
Zone 3
Ratio 2.0
R2 = 0.65
Nitrification of Fertilizers
Soil NO3
Nitrification Manure
δ18ONO3 (‰)
δ15NNO3 (‰)

Figure 4

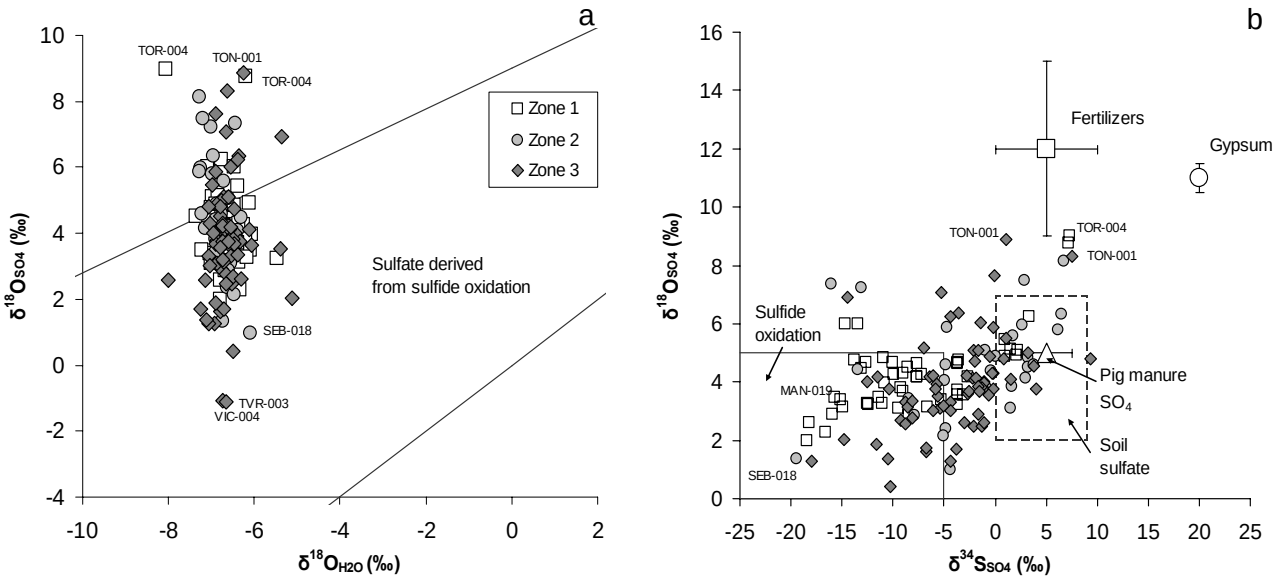

a
b
Zone 1
Zone 2
Zone 3
Sulfate derived
from sulfide oxidation
TOR-004
TON-001
TOR-004
SEB-018
TVR-003
VIC-004
δ18OSO4 (‰)
δ18OH2O (‰)
Fertilizers
Gypsum
TON-001
TOR-004
TON-001
Sulfide
oxidation
MAN-019
SEB-018
Pig manure
SO4
Soil
sulfate
δ34SSO4 (‰)

Figure 5

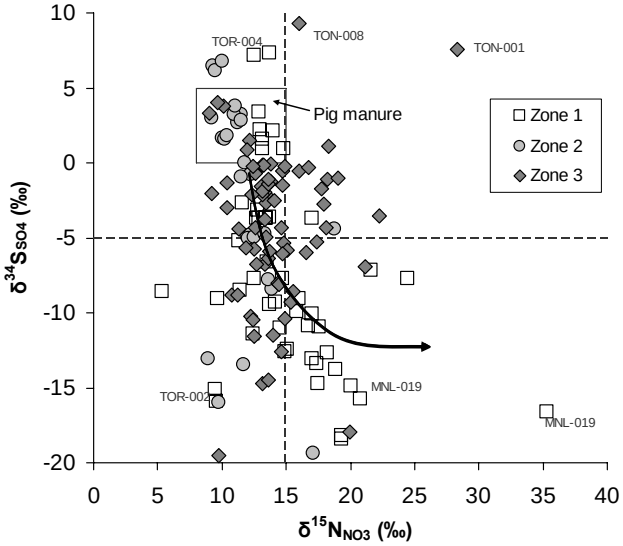

10
5
0
-5
-10
-15
-20
0
5
10
15
20
25
30
35
40
δ34SSO4 (‰)
δ15NNO3 (‰)
TOR-004
TON-008
TON-001
Pig manure
Zone 1
Zone 2
Zone 3
MNL-019
TOR-002
MNL-019

Figure 6

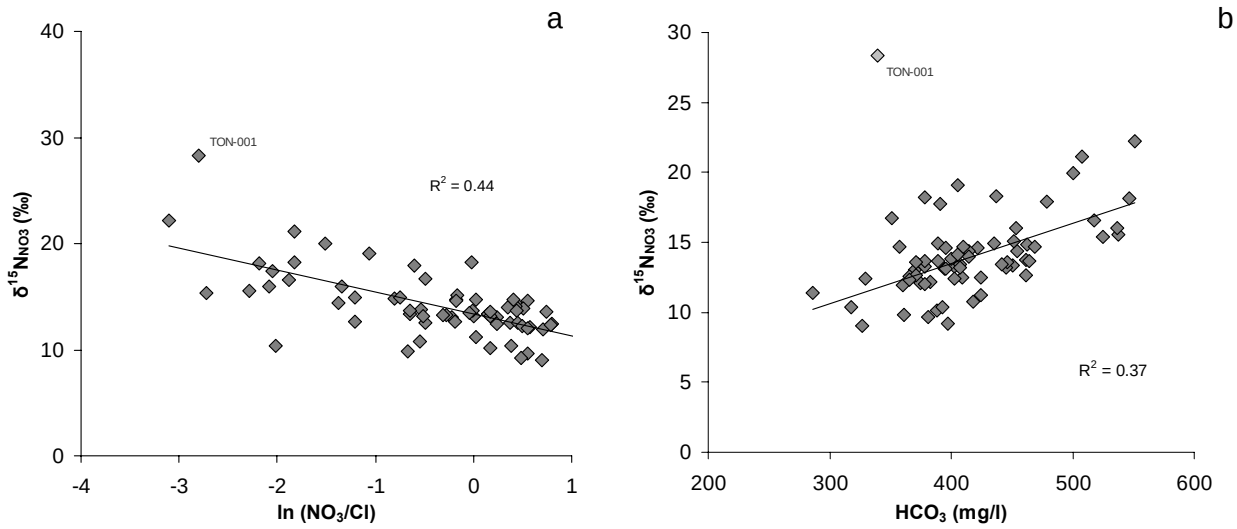


Figure 7

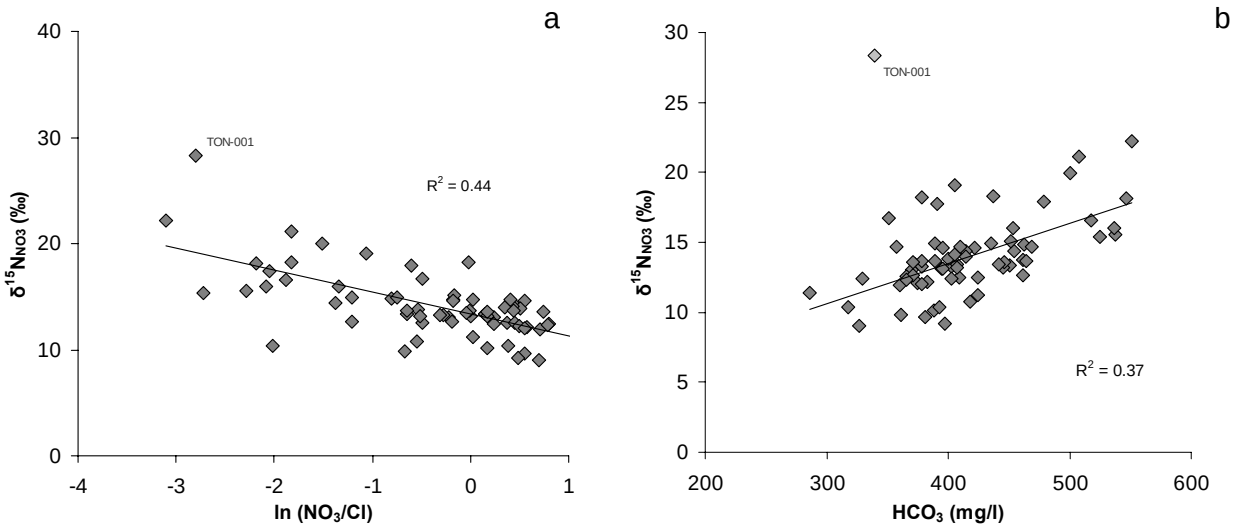


Figure 8

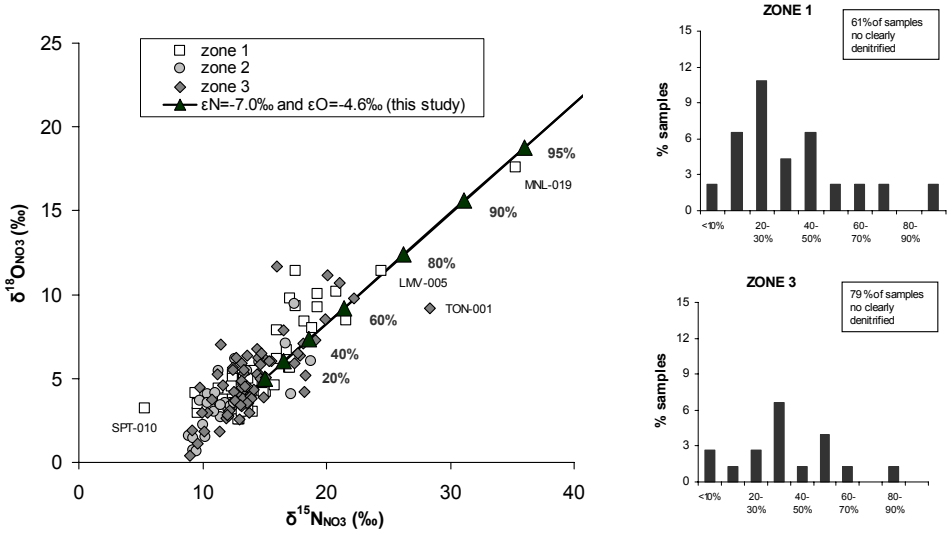

zone 1
zone 2
zone 3
εN=-7.0‰ and εO=-4.6‰ (this study)
95%
90%
80%
60%
40%
20%
MNL-019
LMV-005
TON-001
SPT-010
δ18ONO3 (‰)
δ15NNO3 (‰)
ZONE 1
61%of samples no clearly denitrified
% samples
<10%
20-30%
40-50%
60-70%
80-90%
ZONE 3
79 %of samples no clearly denitrified
% samples
<10%
20-30%
40-50%
60-70%
80-90%

Table 1. Median values of chemical and isotopic data. Groups are distinguished by zone and sampling survey.

	Cond.	DO	Eh	NO_2-	NH_4^+	NO_3^-	HCO_3^-	Cl^-	SO_4^{2+}	Fe	Mn	$\delta^{13}C_{HCO3}$	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$
	µs/cm	mg/l	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(‰)	(‰)	(‰)	(‰)	(‰)
ZONE 1																
APRIL 2005	1114	4.7	361	0.00	0.02	101.5	418.3	54.0	118	n.d.	n.d.	-12.5	-8.1	4.1	13.9	4.3
OCTOBER 2005	960	n.d.	380	0.04	0.02	80.9	419.7	53	118	0.10	0.02	-12.3	-9.3	4.2	13.7	5.0
MAY 2006	914	4.0	417	n.d.	n.d.	125.6	424.6	48	103	0.02	0.02	-11.8	-9.0	4.3	14.8	6.2
ZONE 2																
APRIL 2005	867	5.5	390	0.01	0.02	95.2	369.4	49	67	n.d.	n.d.	-13.2	-0.2	4.7	11.6	3.3
OCTOBER 2005	848	n.d.	n.d.	0.01	0.02	62.2	380.6	46	74	0.12	0.02	-12.0	-1.0	4.1	11.5	3.4
MAY 2006	705	6.6	402	n.d.	n.d.	106.7	390.0	32	69	0.02	0.02	-13.7	2.9	4.6	11.5	4.6
ZONE 3																
APRIL 2005	1396	4.3	370	0.01	0.02	141.2	409.4	111	212	n.d.	n.d.	-12.8	-2.8	4.0	13.5	4.3
OCTOBER 2005	1300	n.d.	375	0.03	0.02	169.6	398.9	109	219	0.08	0.02	-12.4	-4.4	3.8	13.6	3.9
MAY 2006	1475	4.9	407	n.d.	n.d.	176.2	395.3	122	218	0.02	0.02	-12.1	-1.8	3.1	13.6	5.8

n.d.= not determined

Table 2. Estimation of the enrichment factors for N and O associated to the natural denitrification processes.

Sample	$\delta^{15}N\text{-}NO_3$ (‰)		$\delta^{18}O\text{-}NO_3$ (‰)		NO_3 (ppm)		$\varepsilon\ ^{15}N$ (‰)	$\varepsilon\ ^{18}O$ (‰)
	apr-05	oct-05	apr-05	oct-05	apr-05	oct-05		
LMV005	21.6	24.4	8.5	11.4	116.0	77.7	-7.0	-7.4
MAL001	14.8	21.1	6.3	10.7	118.4	46.0	-6.7	-4.6
SEB015	13.9	18.8	3.9	6.0	178.4	58.5	-4.4	-1.9
SEB017	13.2	20.0	4.5	8.5	156.2	64.4	-7.7	-4.5
ORI001	13.4	17.0	3.6	5.6	63.0	50.0	-15.5	-8.9

Table I. Dataset including the chemical and isotopic data of the 3 surveys (April 2005, October 2005 and May 2006)

well	well depth	Cond.	T[a]	pH	O2	Eh	NO_2^-	NH_4^+	NO_3	HCO_3	Cl	SO_4	Na	Ca	Mg	K	Fe	Mn	$\delta^{13}C_{HCO3}$	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$
	m	µs/cm	°C		mg/l	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
ZONE 1																								
April 2005																								
LMR-011	160	1580	15.2	7.0	4.9	383	0.00	<0,02	139.0	434.8	72.0	177	44	219	50	23	n.d.	n.d.	-13.5	-7.7	4.2	14.7	4.3	-6.7
LMV-005	51	1089	n.d.	7.1	4.8	n.d.	0.07	0.22	116.0	397.2	73.0	96	58	141	36	5	n.d.	n.d.	-12.2	-7.2	4.3	21.6	8.5	-6.3
LMV-009	33	1265	n.d.	6.9	7.7	n.d.	0.00	<0,02	223.0	416.8	71.0	118	34	188	47	10	n.d.	n.d.	-12.4	2.2	5.1	13.0	2.5	-7.0
MNL-018	14	1246	9.7	7.0	16.3	388	0.00	<0,02	120.0	388.4	90.9	188	36	181	42	13	n.d.	n.d.	-12.6	-3.7	4.6	13.4	4.1	-6.9
MNL-019	60	1664	8.7	7.5	4.5	345	1.98	<0,02	102.0	426.5	101.0	397	180	118	52	8	n.d.	n.d.	-10.8	-16.6	2.3	35.3	17.6	-6.3
MNL-027	5	1492	n.d.	6.9	8.3	n.d.	0.00	<0,02	157.8	477.3	121.2	239	33	227	60	14	n.d.	n.d.	-12.6	-12.4	3.2	15.1	4.2	-6.6
ORI-001	n.d.	918	10.9	7.0	1.4	319	0.43	0.22	63.0	443.1	25.4	110	24	144	32	16	n.d.	n.d.	-13.7	-3.7	3.2	13.4	3.6	-5.5
SMC-001	110	1140	10.3	7.4	4.6	387	0.00	0.31	149.0	409.9	53.0	120	25	174	43	3	n.d.	n.d.	-12.5	-6.6	3.2	13.5	4.8	-6.7
SMC-002	115	1162	7.7	6.9	2.7	363	0.00	<0,02	126.0	444.1	56.0	82	26	178	32	4	n.d.	n.d.	-13.7	-3.7	3.6	12.9	5.0	-6.7
SMC-010	120	1006	7.7	7.1	4.5	357	0.04	<0,02	101.0	343.1	55.0	117	28	153	32	8	n.d.	n.d.	-12.3	-10.9	4.0	16.8	6.7	-6.1
SMC-024	28	852	7.9	7.3	7.3	344	0.00	<0,02	50.9	345.5	40.4	93	20	135	26	6	n.d.	n.d.	-11.3	-9.9	4.3	15.8	4.6	-6.4
SMC-025	80	827	12.5	7.2	7.7	364	0.03	<0,02	21.6	396.3	18.3	95	19	125	30	6	n.d.	n.d.	-12.6	-13.1	4.5	17.0	9.8	-7.1
SMC-037	67	892	14.3	7.3	8.6	351	0.00	0.02	30.6	419.7	29.2	100	25	131	34	3	n.d.	n.d.	-12.3	-12.7	4.7	18.2	8.4	-6.7
SPT-001	100	907	13.5	7.0	2.7	355	0.14	<0,02	38.1	409.9	53.0	120	18	142	37	5	n.d.	n.d.	-12.5	-18.2	2.6	19.3	9.3	-6.8
SPT-010	200	751	9.0	7.0	3.1	357	0.03	<0,02	14.1	474.3	10.0	67	24	132	27	2	n.d.	n.d.	-14.1	-8.6	4.5	5.3	3.2	-7.4
SVT-004	20	1491	11.4	6.8	5.6	341	0.05	0.12	208.0	557.8	118.5	91	28	292	20	5	n.d.	n.d.	-6.9	2.1	4.9	14.0	3.0	-6.1
TOR-002	3	1138	11.0	7.1	5.0	461	0.00	<0,02	68.5	438.2	36.2	332	23	185	45	5	n.d.	n.d.	-14.0	-15.1	3.4	9.5	4.1	-7.0
TOR-004	47	735	11.1	7.4	4.5	409	0.00	<0,02	22.6	240.6	25.8	78	16	101	14	3	n.d.	n.d.	-12.1	7.3	9.0	13.7	3.1	-8.1
TOR-009	65	1190	8.0	7.3	1.6	404	0.03	<0,02	154.0	449.0	60.0	144	23	202	41	6	n.d.	n.d.	-12.9	-5.2	3.4	11.3	4.4	-6.6
TOR-013	70	1080	12.9	6.9	3.3	361	0.00	<0,02	84.0	386.0	32.3	148	17	161	39	3	n.d.	n.d.	-11.8	-8.5	2.9	11.4	3.7	-6.7
October 2005																								
LMR-011	160	1994	16.1	6.8	n.d.	420	0.04	<0,02	267.6	419.7	120	201	37	239	49	31	0.074	< 0.02	-14.1	-3.6	4.7	13.7	4.0	-6.6
LMV-005	51	1036	16.3	7.4	n.d.	459	0.10	<0,02	77.7	424.6	76	106	74	123	32	5	0.074	< 0.02	-12.3	-7.7	4.6	24.4	11.4	-6.1
LMV-009	33	1109	14.6	7.1	n.d.	419	0.03	<0,02	181.0	408.9	61	108	32	169	42	9	0.063	< 0.02	-11.4	3.4	6.2	12.9	2.5	-6.5
MNL-018	14	1153	15.0	7.0	n.d.	405	0.04	0.02	220.0	360.1	68	188	32	191	43	11	0.103	< 0.02	-12.3	-2.7	4.2	11.6	3.7	-6.3
MNL-019	60	1106	16.2	7.1	n.d.	352	0.34	<0,02	82.3	422.1	67	284	92	125	52	8	0.166	< 0.02	-9.3	-15.7	3.5	20.8	10.2	-6.6
MNL-027	5	1262	17.5	6.9	n.d.	356	0.02	<0,02	155.9	488.0	86	244	33	219	59	15	0.104	< 0.02	-11.5	-12.6	3.3	14.9	4.2	-6.1
ORI-001	n.d.	960	16.3	7.1	n.d.	301	0.10	<0,02	50.0	450.4	24	144	24	133	30	23	0.131	< 0.02	-12.7	-3.7	4.7	17.0	5.6	-6.7
SMC-001	110	840	n.d.	7.3	n.d.	n.d.	<0,01	<0,02	78.3	405.0	38	109	27	125	40	2	0.145	< 0.02	-10.2	-9.3	3.8	14.1	5.5	-6.7
SMC-002	115	936	n.d.	6.9	n.d.	n.d.	<0,01	<0,02	135.9	439.2	53	84	23	181	32	3	0.132	< 0.02	-13.4	-3.1	3.6	12.7	4.7	-6.9
SMC-010	120	907	n.d.	7.0	n.d.	n.d.	<0,01	<0,02	143.1	390.4	56	114	26	174	32	8	0.109	< 0.02	-13.1	-9.4	3.1	13.7	5.0	-6.7
SMC-024	28	747	n.d.	6.8	n.d.	n.d.	<0,01	<0,02	56.4	400.2	40	103	19	122	31	6	0.095	< 0.02	-13.0	-10.1	4.7	17.0	5.7	-6.6
SMC-025	80	892	n.d.	6.7	n.d.	n.d.	<0,01	<0,02	25.5	475.8	23	111	29	161	32	8	0.076	< 0.02	-12.2	-11.0	4.9	17.5	11.4	-6.5
SMC-037	67	780	16.1	7.0	n.d.	341	<0,01	<0,02	35.2	419.7	30	105	24	127	34	2	0.068	< 0.02	-11.4	-13.8	4.8	18.8	8.0	-7.3
SPT-001	100	807	16.9	7.0	n.d.	365	0.09	<0,02	33.3	405.0	20	132	16	131	34	4	0.102	< 0.02	-11.2	-18.4	2.0	19.3	10.0	-6.4
SVT-004	20	1247	15.1	6.8	n.d.	378	0.07	<0,02	191.7	536.8	83	98	28	261	20	5	0.083	< 0.02	-7.4	1.6	5.1	13.2	3.0	-6.1
TOR-002	3	1049	15.0	7.0	n.d.	404	0.06	<0,02	68.6	430.4	25	248	23	179	44	6	0.114	< 0.02	-13.4	-15.9	2.9	9.6	2.9	-6.5
TOR-004	47	554	15.2	7.4	n.d.	375	0.02	<0,02	36.0	234.2	43	118	14	82	11	2	0.290	< 0.02	-11.3	7.1	8.8	12.5	3.8	-8.0
TOR-009	65	1166	18.0	6.9	n.d.	427	0.02	<0,02	161.1	450.9	72	151	26	204	42	6	0.078	< 0.02	-12.7	-7.7	4.2	12.5	4.9	-6.3
TOR-013	70	948	15.3	6.9	n.d.	381	0.02	<0,02	80.9	383.1	33	165	16	157	38	3	0.080	< 0.02	-12.7	-11.4	3.5	12.4	5.2	-6.5

Table I. (continued)

well	well depth	Cond.	T[a]	pH	O2	Eh	NO_2^-	NH_4^+	NO_3	HCO_3	Cl	SO_4	Na	Ca	Mg	K	Fe	Mn	$\delta^{13}C_{HCO3}$	$\delta^{34}S_{SO4}$	$\delta^{18}o_{SO4}$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$
	m	µs/cm	ºC		mg/l	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
May 2006																								
LMV 009	33	1337	15.2	6.9	7.6	420	n.d.	n.d.	252.5	412.4	73	117	32	210	53	9	< 0.02	< 0.02	-12.5	0.9	4.9	13.2	5.9	-6.9
MAN 019	60	1275	16.0	7.1	1.7	310	n.d.	n.d.	240.8	429.4	86	332	191	123	57	8	0.122	< 0.02	-11.4	-14.9	3.1	20.1	11.2	-6.4
SMC 002	115	914	16.2	6.8	0.8	343	n.d.	n.d.	125.6	439.2	52	81	25	194	36	4	< 0.02	< 0.02	-12.3	-3.7	3.7	12.7	6.2	-6.4
SMC 010	120	880	16.4	7.0	1.1	357	n.d.	n.d.	151.7	341.6	48	116	30	178	39	6	0.049	< 0.02	-11.8	-11.0	3.3	14.5	6.2	-6.2
SMC 025	28	634	18.4	7.1	6.8	426	n.d.	n.d.	17.0	390.4	18	92	21	125	35	4	< 0.02	< 0.02	-11.2	-13.4	4.3	16.0	11.7	-7.1
SMC 024	80	741	15.6	7.1	5.7	441	n.d.	n.d.	44.1	392.8	28	81	17	151	29	6	< 0.02	< 0.02	-9.2	-9.0	6.0	17.4	5.9	-6.4
SMC 037	67	697	17.7	6.9	1.0	356	n.d.	n.d.	31.6	424.6	30	103	25	145	38	2	< 0.02	< 0.02	-12.1	-14.7	6.0	17.5	9.3	-6.5
SVT 004	20	1489	14.4	6.7	4.0	417	n.d.	n.d.	223.2	558.8	118	83	29	309	23	4	0.078	< 0.02	-11.6	1.0	5.4	14.8	4.7	-6.4
TOR 002	3	1214	15.9	7.0	5.8	441	n.d.	n.d.	87.6	427.0	28	242	25	210	53	5	< 0.02	< 0.02	-14.3	-9.0	3.7	9.6	3.5	-6.8
ZONE 2																								
April 2005																								
CDT-004	60	919	14.0	7.1	1.6	359	0.1	<0,02	150.7	344.0	67	68	17	157	29	2	n.d.	n.d.	-13.1	-4.9	2.4	12.0	3.3	-6.6
CDT-009	70	976	10.3	7.2	4.5	411	0.0	<0,02	129.3	369.9	68	67	18	172	22	3	n.d.	n.d.	-13.4	-0.4	4.4	12.5	3.4	-6.9
CDT-011	90	804	14.0	7.0	2.8	455	0.0	<0,02	43.9	413.3	33	67	14	148	22	1	n.d.	n.d.	-13.7	-4.8	4.6	12.3	3.6	-7.2
FLG-006	45	1091	6.8	7.0	6.0	365	0.0	<0,02	129.2	368.9	55	66	21	192	22	5	n.d.	n.d.	-13.9	3.2	4.8	11.5	2.7	-6.8
FLG-016	15	863	6.9	7.5	5.7	390	0.0	<0,02	81.5	368.9	46	98	14	145	34	4	n.d.	n.d.	-11.8	1.7	3.8	10.0	2.3	-6.9
SEB-015	100	1364	10.6	6.9	1.9	249	0.0	0.12	178.4	426.5	124	165	57	191	49	9	n.d.	n.d.	-12.7	-8.4	3.4	13.9	3.9	-6.9
SJV-004	35	870	11.0	6.8	5.3	400	0.0	<0,02	51.8	442.6	51	60	10	194	11	1	n.d.	n.d.	-15.3	2.7	6.0	11.2	5.4	-7.2
TAR-004	23	738	6.9	n.d.	5.6	n.d.	0.0	<0,02	109.0	233.3	42	54	17	129	9	1	n.d.	n.d.	-15.5	6.5	6.3	9.2	0.7	-7.0
TVR-006	180	620	9.0	7.4	5.6	355	0.0	<0,02	21.1	315.8	18	68	13	115	16	2	n.d.	n.d.	-12.4	-13.1	7.2	8.9	1.6	-7.0
TVR-008	30	856	n.d.	7.1	5.9	404	0.0	0.02	80.0	390.9	27	57	14	155	21	2	n.d.	n.d.	-13.0	0.0	4.9	11.8	3.5	-6.9
October 2005																								
CDT-004	60	876	n.d.	6.8	n.d.	n.d.	<0,01	<0,02	144.4	361.1	50	72	15	150	29	2	0.245	< 0.02	-12.5	-5.0	2.1	12.1	3.1	-6.8
CDT-009	70	936	n.d.	6.7	n.d.	n.d.	<0,01	<0,02	138.2	380.6	60	74	19	171	23	3	0.081	< 0.02	-12.4	-0.8	3.8	12.3	3.4	-6.7
CDT-011	90	715	n.d.	6.8	n.d.	n.d.	<0,01	<0,02	35.7	405.0	22	67	14	127	22	1	0.087	< 0.02	-12.0	-4.9	4.1	12.5	3.6	-7.2
FLG-006	45	1039	n.d.	6.7	n.d.	n.d.	<0,01	<0,02	227.9	373.3	64	90	19	199	24	7	0.108	< 0.02	-13.8	3.3	4.5	10.9	3.0	-6.8
FLG-016	15	848	n.d.	6.9	n.d.	n.d.	0.03	<0,02	92.0	380.6	46	103	14	146	33	3	0.123	< 0.02	-13.1	1.6	3.1	10.2	1.5	-6.5
SEB-015	100	1419	n.d.	7.5	n.d.	n.d.	3.89	<0,02	58.5	575.8	127	234	310	59	16	5	0.423	0.027	-11.6	-4.4	1.0	18.8	6.0	-7.0
SEB-018	60	1400	n.d.	7.0	n.d.	n.d.	1.56	0.40	10.4	502.2	138	277	296	53	21	4	0.121	< 0.02	-11.9	-19.4	1.4	17.1	4.0	-6.6
SJV-004	35	781	n.d.	6.6	n.d.	n.d.	0.02	<0,02	45.1	451.4	29	51	8	174	10	< 1	0.083	< 0.02	-11.0	1.8	5.6	10.4	4.1	-6.3
TAR-004	23	674	15.8	6.8	n.d.	322	0.00	0.02	104.2	256.2	33	54	15	126	9	1	0.214	< 0.02	-13.4	6.2	5.8	9.5	0.7	-6.9
TVR-006	180	598	n.d.	7.1	n.d.	n.d.	<0,01	0.02	24.6	307.4	13	87	14	110	16	1	0.154	< 0.02	-11.4	-16.0	7.3	9.8	3.7	-7.0
TVR-008	30	713	n.d.	6.8	n.d.	n.d.	<0,01	0.02	62.2	376.2	22	53	18	130	19	2	0.101	< 0.02	-10.8	-1.0	5.1	11.5	3.4	-6.8
May 2006																								
CDT 011	90	700	16.8	6.9	3.8	451	n.d.	n.d.	42.1	414.8	26	69	14	153	28	1	< 0.02	< 0.02	-13.7	-4.7	5.9	13.3	5.5	-7.3
FLG 006	45	983	17.1	6.9	6.1	402	n.d.	n.d.	253.7	356.2	57	91	19	229	28	5	0.031	< 0.02	-14.3	3.8	4.6	11.0	4.2	-6.8
FLG 016	15	810	17.6	7.3	6.9	382	n.d.	n.d.	148.4	336.7	33	84	14	168	37	3	< 0.02	< 0.02	-12.5	3.0	4.1	9.2	1.4	-7.1
SEB 015	100	1121	17.6	6.9	4.8	378	n.d.	n.d.	267.4	427.0	98	172	90	215	55	5	< 0.02	< 0.02	-10.1	-7.8	2.9	13.6	6.4	-6.6
SJV 004	35	705	15.7	6.8	8.6	471	n.d.	n.d.	57.9	461.2	32	65	11	212	13	< 1	< 0.02	< 0.02	-13.7	2.9	7.5	11.5	7.0	-7.2
TAR 004	23	625	15.3	6.5	7.9	469	n.d.	n.d.	106.7	231.8	27	50	16	133	10	< 1	0.082	< 0.02	-14.3	6.8	8.1	10.0	2.9	-7.3
TAV 008	30	683	13.8	7.0	6.6	390	n.d.	n.d.	102.1	390.0	28	57	12	171	23	2	0.030	< 0.02	-11.7	-13.5	4.4	11.7	4.6	-6.9

Table I. (continued)

well	well depth	Cond.	T[a]	pH	O2	Eh	NO_2^-	NH_4^+	NO_3	HCO_3	Cl	SO_4	Na	Ca	Mg	K	Fe	Mn	$\delta^{13}C_{HCO3}$	$\delta^{34}S_{SO4}$	$\delta^{18}o_{SO4}$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$
	m	µs/cm	ºC		mg/l	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
ZONE 3																								
April 2005																								
BAL-001	n.d.	1015	14.8	7.1	5.7	392	0.0	0.02	180.0	388.4	87	44	20	166	38	0	n.d.	n.d.	-12.8	3.8	4.5	10.1	1.8	-6.8
BAL-005	30	1034	13.6	6.9	9.3	408	0.0	<0,02	101.9	418.2	101	145	32	168	49	3	n.d.	n.d.	-14.1	-8.8	3.3	10.8	3.7	-7.1
FLG-019	20	1351	12.4	6.9	4.3	362	0.0	0.02	141.2	461.6	138	141	64	216	25	10	n.d.	n.d.	-14.3	-0.1	7.6	13.8	3.0	-6.9
GRB-007	60	1150	10.7	7.1	3.2	376	0.0	0.02	160.0	373.3	79	116	48	175	31	8	n.d.	n.d.	-12.9	-2.1	5.1	13.4	3.8	-6.7
GRB-101	17	1318	12.9	7.0	8.0	383	0.0	<0,02	191.8	370.4	137	224	44	206	58	4	n.d.	n.d.	-12.5	-1.6	2.9	13.0	2.6	-6.8
GRB-106	70	1022	13.6	7.3	8.9	344	0.2	<0,02	127.2	378.2	74	162	44	137	43	23	n.d.	n.d.	-12.3	-1.1	4.0	18.2	4.2	-6.4
GRB-111	50	1733	9.6	6.8	5.5	218	0.0	<0,02	124.0	444.1	136	274	53	221	67	11	n.d.	n.d.	-12.3	-6.8	1.6	13.4	3.7	-6.8
GRB-112	14	1387	11.4	7.2	5.3	347	0.0	<0,02	202.7	409.4	80	212	36	209	48	24	n.d.	n.d.	-13.3	-5.8	3.9	12.5	5.6	-6.7
GRB-113	11	1652	10.2	7.0	3.6	321	0.0	0.12	396.0	360.1	111	169	39	238	67	15	n.d.	n.d.	-12.1	-5.7	3.5	11.9	2.6	-5.4
GRB-115	6	1313	9.4	7.2	7.8	396	0.0	<0,02	142.3	402.6	108	240	41	188	62	5	n.d.	n.d.	-12.6	-2.0	4.7	13.3	5.3	-6.5
GRB-117	8	1580	12.8	6.9	12.0	361	0.1	0.02	302.0	407.5	145	180	40	242	49	5	n.d.	n.d.	-12.5	-2.7	3.6	13.5	4.0	-6.5
GRB-118	52	1615	13.0	7.1	4.0	364	0.0	0.02	299.0	422.1	99	197	70	228	49	10	n.d.	n.d.	-12.3	-4.3	3.3	14.6	5.2	-6.6
GRB-119	11	1412	10.4	6.8	6.9	388	0.0	0.02	321.3	394.3	145	186	40	244	52	7	n.d.	n.d.	-12.8	-2.2	4.1	13.1	4.1	-6.6
MAL-001	12	1850	13.0	7.3	1.6	372	0.0	<0,02	118.4	462.6	152	462	85	213	105	11	n.d.	n.d.	-12.9	-5.4	3.1	14.8	6.3	-6.9
MAL-003	7	1560	7.2	7.0	3.5	360	0.0	<0,02	127.0	464.1	139	321	60	219	73	11	n.d.	n.d.	-13.9	-6.4	4.2	13.6	3.8	-6.8
SCV-003	5	1300	11.9	6.9	6.7	415	0.0	0.12	144.1	450.4	71	208	26	202	54	3	n.d.	n.d.	-12.9	-3.7	1.7	13.3	4.3	-6.7
SEB-017	9	1345	10.9	6.9	2.4	370	0.0	<0,02	156.2	445.5	89	216	32	231	46	3	n.d.	n.d.	-12.9	-14.8	2.0	13.2	4.5	-5.1
TAR-003	45	1427	8.8	7.4	7.5	361	0.0	<0,02	100.1	424.6	93	276	106	146	56	4	n.d.	n.d.	-11.5	-11.6	1.9	12.5	4.2	-6.9
TON-001	35	2370	11.6	7.1	2.9	370	0.1	0.60	18.2	339.2	171	968	119	314	110	15	n.d.	n.d.	-11.4	7.5	8.3	28.3	9.2	-6.6
TON-002	n.d.	841	12.9	7.4	6.2	415	0.0	0.02	124.2	327.0	35	52	16	125	30	2	n.d.	n.d.	-11.9	3.3	5.0	9.0	0.4	-6.8
TON-006	n.d.	2930	13.2	6.9	2.1	378	0.0	<0,02	102.4	537.3	574	491	228	270	124	7	n.d.	n.d.	-13.7	-8.6	3.1	15.6	6.0	-6.7
TON-007	16	2330	13.6	6.9	2.8	359	0.1	<0,02	166.6	454.3	378	495	135	272	131	11	n.d.	n.d.	-13.2	-8.1	2.8	14.4	5.2	-6.7
TON-008	32	2240	13.1	7.0	3.2	176	0.0	0.12	76.0	436.8	269	586	159	244	93	18	n.d.	n.d.	-13.0	1.1	5.5	18.3	5.2	-7.0
TVR-003	75	1133	9.1	7.1	6.8	386	0.0	<0,02	159.0	374.8	51	76	25	191	32	4	n.d.	n.d.	-12.8	1.5	4.1	12.1	2.8	-6.7
VIC-004	70	2290	8.4	7.3	2.7	251	0.2	0.02	260.5	405.5	429	316	226	206	74	8	n.d.	n.d.	-11.0	-1.0	4.0	19.1	7.3	-6.8
VIC-007	30	1396	10.8	7.1	6.4	393	0.0	0.02	100.1	478.7	105	309	52	209	70	10	n.d.	n.d.	-13.0	-2.8	4.2	17.9	6.4	-6.8
VIC-019	140	1133	9.2	7.4	1.1	348	0.0	<0,02	98.1	389.4	118	167	52	161	53	4	n.d.	n.d.	-12.4	-10.4	3.7	14.9	5.0	-6.8
VIC-100	40	1103	11.5	7.0	3.6	383	0.0	<0,02	127.4	357.7	87	121	32	171	31	7	n.d.	n.d.	-12.9	-0.5	4.9	14.7	5.0	-6.9
VIC-103	12	1760	8.9	6.9	2.4	270	0.0	0.12	16.8	551.0	214	345	102	220	76	4	n.d.	n.d.	-12.3	-3.6	6.4	22.2	9.8	-6.4
October 2005																								
BAL-001	n.d.	883	14.4	7.0	n.d.	359	<0,01	0.02	169.6	380.6	56	41	17	150	35	< 1	0.076	< 0.02	-11.3	4.0	3.7	9.6	1.1	-6.8
BAL-005	30	1010	15.4	7.0	n.d.	402	0.02	<0,02	64.2	361.1	72	237	38	157	47	3	0.076	< 0.02	-11.9	-19.5	n.d.	9.8	4.5	-6.7
FLG-019	20	1119	n.d.	6.6	n.d.	n.d.	<0,01	<0,02	149.7	407.5	143	179	62	193	23	8	0.078	< 0.02	-13.6	-0.2	5.9	13.2	3.4	-6.2
GRB-007	60	n.d.	15.1	7.0	n.d.	439	0.05	<0,02	204.2	378.2	160	163	94	184	32	10	0.073	< 0.02	-13.9	-0.2	4.3	13.3	3.8	-6.5
GRB-101	17	1367	16.6	6.9	n.d.	347	0.03	<0,02	197.7	378.2	114	270	50	217	62	5	0.053	< 0.02	-13.2	-5.9	n.d.	13.7	3.5	-7.0
GRB-106	70	1137	15.5	7.0	n.d.	397	0.06	<0,02	174.5	397.7	61	189	43	163	48	14	0.062	< 0.02	-12.9	-2.1	2.5	9.2	1.9	-6.8
GRB-111	50	1685	18.0	7.1	n.d.	467	1.79	0.02	211.9	461.2	407	211	137	270	68	8	0.327	0.100	-13.4	-6.8	1.7	12.7	3.7	-6.5
GRB-112	14	1224	13.6	7.1	n.d.	335	0.03	<0,02	169.7	414.8	63	227	38	189	49	20	0.071	< 0.02	-13.5	-8.1	3.4	14.4	6.8	-7.0
GRB-113	11	1367	14.6	7.1	n.d.	364	0.03	<0,02	522.2	286.0	74	98	30	212	52	11	0.073	< 0.02	-11.8	-4.4	3.0	11.4	1.8	-6.8
GRB-115	6	1132	15.0	7.0	n.d.	375	0.11	0.02	153.0	395.3	74	233	35	181	59	5	0.077	< 0.02	-12.4	-1.9	4.1	13.1	4.9	-6.5
GRB-117	8	n.d.	15.2	6.8	n.d.	460	0.03	<0,02	322.9	400.2	111	165	36	241	49	6	0.110	< 0.02	-11.9	-1.3	3.8	13.8	3.9	-6.8
GRB-118	52	n.d.	14.9	6.9	n.d.	399	0.05	<0,02	286.0	405.0	106	178	40	233	47	9	0.111	< 0.02	-12.5	-2.5	3.7	14.1	4.4	-6.6

Table I. (continued)

well	well depth	Cond.	T[a]	pH	O2	Eh	NO_2^-	NH_4^+	NO_3	HCO_3	Cl	SO_4	Na	Ca	Mg	K	Fe	Mn	$\delta^{13}C_{HCO3}$	$\delta^{34}S_{SO4}$	$\delta^{18}o_{SO4}$	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$
	m	µs/cm	ºC		mg/l	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
GRB-119	11	1840	14.4	6.9	n.d.	430	0.07	<0,02	303.2	366.0	111	141	32	225	47	5	0.088	< 0.02	-12.6	-0.7	3.6	12.6	3.7	-6.2
MAL-001	12	1558	14.1	6.9	n.d.	321	0.04	<0,02	46.0	507.5	162	524	118	205	102	9	0.077	< 0.02	-12.8	-6.9	5.2	21.1	10.7	-6.4
MAL-003	7	1267	16.2	7.0	n.d.	378	0.00	<0,02	151.0	451.4	102	263	55	198	65	7	0.079	< 0.02	-14.1	-5.8	3.8	15.1	5.1	-6.4
SCV-003	5	1138	13.9	6.9	n.d.	436	0.03	<0,02	114.8	446.5	55	211	24	206	51	3	1.48	0.042	-11.5	-14.5	6.9	13.6	4.5	-6.7
SEB-017	9	1300	n.d.	7.0	n.d.	n.d.	0.02	<0,02	64.4	500.7	167	239	192	148	31	4	0.068	< 0.02	-10.8	-17.9	1.3	20.0	8.5	-6.4
TAR-003	45	1336	16.0	7.2	n.d.	398	0.01	<0,02	278.0	383.1	97	248	88	172	64	5	0.106	< 0.02	-10.7	-10.3	0.4	12.2	3.1	-6.9
TON-001	35	1683	14.5	7.0	n.d.	335	<0,01	<0,02	34.9	317.2	149	832	129	249	98	8	0.083	< 0.02	-10.4	-3.0	2.6	10.4	3.0	-6.1
TON-006	n.d.	2700	15.4	7.1	n.d.	364	0.05	0.07	72.2	524.6	626	445	285	255	115	8	0.080	< 0.02	-12.4	-9.3	2.7	15.4	6.0	-6.7
TON-007	16	2630	14.9	7.0	n.d.	299	0.29	1.17	123.3	517.3	464	650	220	274	149	16	0.070	< 0.02	-13.2	-6.0	4.2	16.6	7.9	-5.4
TON-008	32	1487	13.9	6.7	n.d.	183	0.01	0.12	87.5	435.3	168	482	116	211	81	15	0.076	< 0.02	-12.2	-0.2	4.3	14.9	3.9	-6.9
TVR-003	75	1040	n.d.	6.7	n.d.	n.d.	<0,01	<0,02	203.5	378.2	67	101	27	189	31	4	0.080	< 0.02	-12.2	0.9	4.8	12.0	2.8	-6.7
VIC-004	70	2030	15.1	7.0	n.d.	229	0.14	<0,02	332.8	391.4	315	304	179	225	69	5	0.096	< 0.02	-11.3	-1.7	3.8	17.7	6.5	-6.5
VIC-007	30	1027	n.d.	7.0	n.d.	n.d.	0.01	<0,02	98.1	389.4	85	157	49	138	47	4	0.080	< 0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
VIC-019	140	1130	n.d.	6.7	n.d.	n.d.	0.03	<0,02	183.9	414.8	74	168	35	197	38	7	0.082	< 0.02	-12.4	-11.5	4.2	14.0	3.8	-6.5
VIC-100	40	1103	n.d.	6.7	n.d.	n.d.	<0,01	<0,02	190.5	388.9	70	153	35	189	35	7	0.118	< 0.02	-12.5	-1.4	6.0	13.6	3.6	-6.6
VIC-103	12	1449	n.d.	6.1	n.d.	n.d.	<0,01	0.07	34.7	546.6	175	332	106	195	68	4	1.42	0.048	-11.2	-4.4	6.2	18.1	7.1	-6.4
May 2006																								
BAL 005	n.d.	1060	15.3	7.2	8.6	422	n.d.	n.d.	152.5	424.6	85	151	32	189	57	3	< 0.02	< 0.02	-13.8	-8.8	2.6	11.2	5.2	-7.1
GRB 106	70	1330	15.5	6.9	5.2	450	n.d.	n.d.	188.8	392.8	74	184	41	191	54	17	0.091	< 0.02	-12.8	-1.3	2.5	10.4	3.6	-6.6
GRB 111	50	1554	15.0	6.9	4.9	490	n.d.	n.d.	225.7	370.9	156	192	58	234	63	8	0.067	< 0.02	-12.1	-4.3	1.3	12.6	6.2	-7.1
GRB 117	8	1604	14.7	6.9	6.1	388	n.d.	n.d.	390.4	370.9	107	163	38	282	59	5	< 0.02	< 0.02	-13.2	-1.1	2.6	13.6	5.4	-6.3
GRB 118	52	1676	14.9	6.9	5.0	448	n.d.	n.d.	375.2	409.9	143	186	46	281	58	13	< 0.02	< 0.02	-7.6	-1.5	3.7	14.7	6.5	-6.5
GRB 119	11	1746	14.7	6.9	6.7	427	n.d.	n.d.	528.9	329.4	137	170	39	302	63	4	< 0.02	< 0.02	-12.8	-0.2	3.7	12.4	5.5	-6.6
MAL 003	7	1280	17.0	6.9	5.2	433	n.d.	n.d.	163.6	441.6	98	305	55	234	79	9	< 0.02	< 0.02	-13.1	-5.0	3.2	13.5	4.5	-6.7
TAR 003	45	1272	19.5	7.2	n.d.	416	n.d.	n.d.	207.8	402.6	94	244	104	176	66	4	0.021	< 0.02	-10.0	-10.4	1.4	12.4	5.0	-7.1
TON 001	35	1890	16.6	6.9	0.9	395	n.d.	n.d.	29.6	341.6	150	997	131	354	120	14	0.023	< 0.02	-10.9	1.1	8.9	n.d.	n.d.	-6.3
TON 006	n.d.	2380	17.0	6.8	5.3	399	n.d.	n.d.	99.4	536.8	455	488	227	287	130	9	< 0.02	< 0.02	-13.0	-0.6	3.6	16.0	7.9	-6.8
TON 008	32	1780	14.8	6.8	1.9	116	n.d.	n.d.	89.1	453.8	196	580	157	273	108	20	< 0.02	< 0.02	-12.0	9.3	4.8	16.0	6.2	-7.1
TAV 003	75	1019	14.6	6.9	4.5	414	n.d.	n.d.	256.4	366.0	67	100	28	219	37	4	< 0.02	< 0.02	-12.3	-2.1	-1.1	12.3	4.5	-6.7
VIC 004	70	2480	16.0	7.0	4.6	317	n.d.	n.d.	529.4	351.4	495	304	252	282	91	6	0.038	< 0.02	-10.3	-0.3	-1.1	16.7	7.1	-6.7
VIC 007	30	1371	13.9	6.8	1.1	223	n.d.	n.d.	132.1	468.5	73	388	56	248	88	11	0.513	0.049	-12.2	-6.1	3.0	14.7	5.8	-7.0
VIC 019	140	891	16.6	6.9	1.3	369	n.d.	n.d.	117.0	395.3	80	162	47	168	56	4	< 0.02	< 0.02	-11.3	-12.6	4.0	14.6	5.9	-6.9
VIC 103	12	1395	16.2	6.9	4.0	252	n.d.	n.d.	39.2	n.d.	175	344	99	225	78	4	0.572	0.057	-11.6	-5.3	7.1	17.4	9.4	-6.7

n.d. = not determined